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Selective C-H Bond Cleavage in Methane by Small Gold Clusters

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Abstract: Methane represents the major constituent of natural gas. It is primarily used only as a source of energy by means of combustion, but could also serve as an abundant hydrocarbon feedstock for high quality chemicals. One of the major challenges in catalysis research nowadays is therefore the development of materials that selectively cleave one of the four C-H-bonds of methane and make it thus amenable for further chemical conversion to more valuable compounds. Employing infrared spectroscopy and first-principles calculations it is uncovered herein that the interaction of methane with small gold cluster cations leads to selective C-H-bond dissociation and the formation of hydrido-methyl complexes $\text{H-Au}_x\text{-CH}_3$. The unique selectivity offered by these gold clusters originates from a fine interplay between the closed-shell nature of the gold d-bands and relativistic effects in gold. Such fine balance in fundamental interactions could prove a ‘tunable’ feature in rational catalyst design.

Methane is an important feedstock for the production of more valuable chemical products such as methanol or higher hydrocarbons, but due to its robust chemical structure it is in current industrial processes first turned into syngas (CO , CO_2 and H_2) before larger chemicals are formed.^[1] This indirect, and energy inefficient step could be bypassed if methane could be functionalized directly through the selective activation of the thermodynamically strong C-H bonds. Their high bond dissociation energy of 440 kJ/mol,^[2] typically requires either high reaction temperatures or highly reactive catalysts. Under such severe reaction conditions, the conversion of methane is often not selective and leads to the complete dehydrogenation or the oxidation to carbon monoxide and carbon dioxide.^[3] Thus, the development of novel catalytic materials, which selectively activate and convert methane at low temperatures, represents one of the great challenges in catalysis research today. For the rational design of such catalytic materials, a molecular level understanding of the bond activation, dissociation, and new bond formation mechanisms is mandatory. Towards this goal, free metal atoms as well as small metal and metal-oxide clusters have been shown to represent powerful model systems for the catalytically active sites of heterogeneous catalysts.^[4] Indeed, in recent years experimental and theoretical gas phase studies employing such models achieved significant progress toward a conceptual understanding of methane activation and conversion.^[3b,5]

Recently we demonstrated in a mass spectrometry gas phase experiment that the gold dimer Au_2^+ selectively converts methane to ethylene or formaldehyde in full thermal catalytic cycles.^[6] So far, comparable selective catalytic methane activation reactions have not been observed for any other material and not even for other gold cluster sizes under thermal conditions.^[7] In particular, concurrent theoretical simulations attributed the high product selectivity to the sequential cleavage of single C-H-bonds mediated by Au_2^+ , thus preventing complete dehydrogenation of methane.^[6] In the present contribution, we now employ infrared multiple-photon dissociation (IR-MPD) spectroscopy in conjunction with first-principles spin density functional theory calculations, to gain the first direct insight into the geometrical structure of the gold cluster-methane complexes Au_xCH_4^+ ($x = 2 - 4$). The obtained spectra unambiguously show that in all of these complexes only one single C-H-bond of methane is dissociated, confirming the uniqueness of gold clusters in the selective activation of methane.

Gold clusters are produced via laser ablation of solid gold and reacted with methane in a flow tube reactor before expansion into vacuum, where all species interact with an IR laser and are mass-analyzed in a reflectron time-of-flight mass spectrometer. The gold cluster-methane reaction results in the formation of Au_xCH_4^+ ($x = 2 - 4$) without any indication of methane dehydrogenation in the mass spectrometric analysis. Whenever the IR laser is in resonance with an IR-active vibrational mode of a given Au_xCH_4^+ , multiple photons are sequentially absorbed resulting in heating of the complex until dissociation of the weakest bond occurs and a consequent depletion of the corresponding mass signal. The IR-MPD spectrum of a specific gold cluster-methane complex is recorded by monitoring the ratio of its mass signal with (I) and without (I_0) laser light while varying the laser wavelength. A complicating factor is that methane or its dissociation products are typically rather strongly bound to the gold clusters^[7a] requiring the absorption of a large number of photons to enable dissociation. This complication is circumvented in two complementary ways. To reduce the large number of photons required, Au_xCH_4^+ is labeled with two Ar atoms which, while not perturbing the system, are ejected from the complex upon absorption of only a limited number of IR photons.^[8] Furthermore, in the present investigation, the spectroscopic examination takes place in the cavity of the free electron laser (FELICE)^[9] offering IR intensities that are sufficient to induce dissociation in the gold-methane complexes without the need for messenger atoms. We thus employ two alternative methods that independently provide the

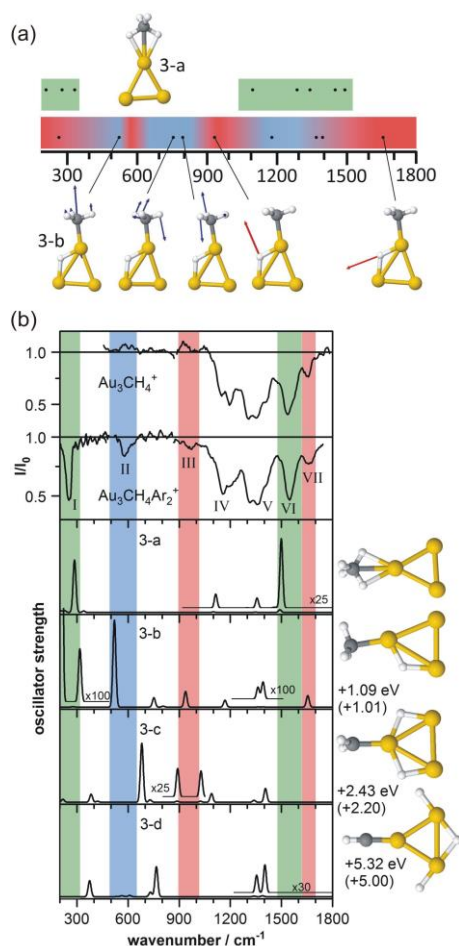


Figure 1. (a) General energy ranges for the vibrational modes of gold cluster-methane complexes. The green, blue, and red regions correspond to motions of CH₄, CH₃, and H units, respectively. The black dots correspond to the modes for two different isomers of Au₃CH₄⁺ and the structures illustrate the nature of the characteristic modes. (b) IR-MPD spectra of Au₃CH₄⁺ and Au₃CH₄Ar₂⁺ (upper two panels) as well as calculated vibrational spectra of different structural isomers of Au₃CH₄⁺. The calculated energies of the isomers (relative to that of the lowest energy one, isomer 3-a) are given next to their structures, with the zero-point-energy-corrected values given in parenthesis. Structural models: Au yellow, C gray, H white.

spectral signatures of Au₃CH₄Ar₂⁺ clusters. To aid in interpreting the experimental spectrum and to gain insight into the C-H bond dissociation properties of the small gold clusters, the IR-MPD spectra are compared with vibrational spectra calculated by use of Born-Oppenheimer spin-density functional theory^[10] with norm-conserving soft pseudopotentials^[11] and the generalized gradient approximation (GGA)^[12] for electronic exchange and correlations.

To identify characteristic vibrational modes of gold-methane complexes, Figure 1a displays the general energy ranges for the vibrational normal modes of a non-dissociated adsorbed CH₄ molecule (green) as well as of the CH₃ group (blue) and the H atom (red) of hydrido-methyl-complexes as deduced from our calculations. The black dots indicate the particular modes of the corresponding isomers of Au₃CH₄⁺ (the modes of further isomeric structures as well as of Au₂CH₄⁺ and Au₄CH₄⁺ can be

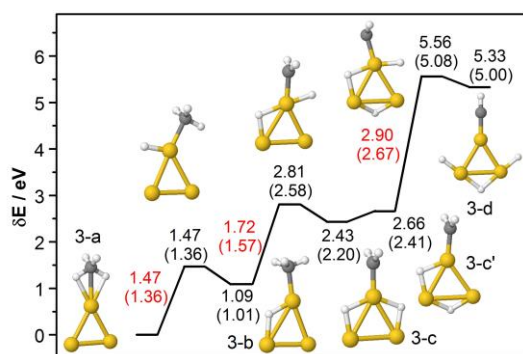


Figure 2. Calculated energy profile for the dissociation of up to three C-H-bonds mediated by Au₃⁺. The black numbers denote the relative energies of the transition states and local minima in eV whereas the red numbers denote the heights of the energy barriers; all values are relative to the energy of the 3-a isomer, and the values in parenthesis correspond to zero-point-energy-corrected values. Structural models: Au yellow, C gray, H white.

found in Figures S1 and S2). The vibrational modes of non-dissociated methane are mainly located below 400 cm^{-1} and between 1000 cm^{-1} and 1500 cm^{-1} while the vibrations of the methyl group and the H atom can be found in the whole energy region between 300 cm^{-1} and 1800 cm^{-1} . Thus, spectral features between 400 cm^{-1} and 1000 cm^{-1} as well as above 1600 cm^{-1} can be regarded as characteristic bands of hydrido-methyl complexes, $\text{H-Au}_x\text{-CH}_3$. This allows for the unambiguous distinction between the different isomeric structures and makes IR-MPD spectroscopy a most suitable method for gaining direct insight into gold-mediated bond cleavage in methane.

These characteristic modes can be found in the experimental IR-MPD spectra detected for the mass of Au_3CH_4^+ and $\text{Au}_3\text{CH}_4\text{Ar}_2^+$, which are shown in Figure 1b and will be discussed below. Both spectra are very similar, indicating that the Ar atoms do not significantly disturb the structure of the gold cluster methane complex. The experimental spectra are compared with the calculated vibrational spectra of four different isomeric structures. The bands I and VI (highlighted in green) can be clearly assigned to the vibrational modes of the non-dissociated methane molecule of isomer 3-a, whereas the spectral features II (blue) and III/ VII (red) can be assigned to motions of the methyl group and the H atom of isomer 3-b, respectively. The bands IV and V arise from the overlap of several modes of isomers 3-a and 3-b which results in the broad but structured nature of these bands. The presence of further higher energy isomers in the experiment can be ruled out due to the absence of the features at 383 cm^{-1} and 681 cm^{-1} (structure 3-c) as well as 375 cm^{-1} and 766 cm^{-1} (structure 3-d) in the experimental spectra. Thus, the IR-MPD spectra clearly demonstrate the coexistence of the two isomeric structures 3-a and 3-b and provide the first direct experimental evidence that the gold trimer is able to selectively facilitate the dissociation of one C-H bond of methane to form a hydrido-methyl complex.

The co-existence of structures 3-a and 3-b is further supported by the calculated reaction profile of the C-H bond dissociation process shown in Figure 2. CH_4 adsorbs on Au_3^+ with a binding (adsorption) energy of 0.76 eV (0.72 eV when

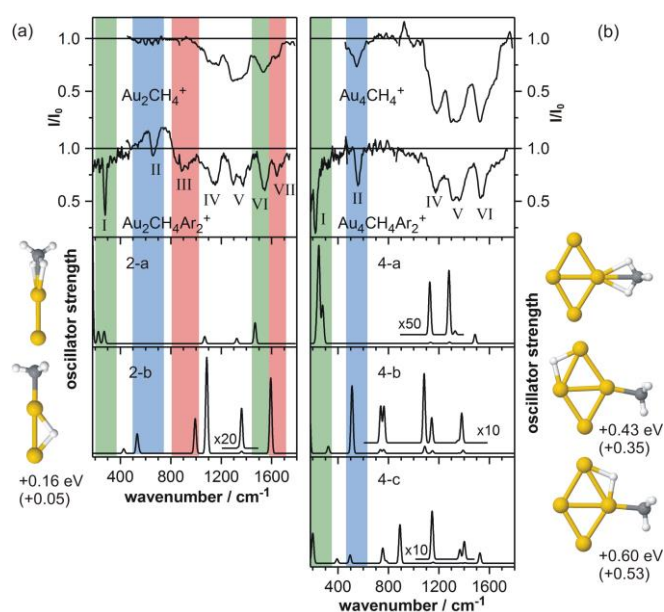


Figure 3. IR-MPD spectra of (a) Au_2CH_4^+ and $\text{Au}_2\text{CH}_4\text{Ar}_2^+$ (upper two panels) as well as of (b) Au_4CH_4^+ and $\text{Au}_4\text{CH}_4\text{Ar}_2^+$ (upper two panels) together with calculated vibrational spectra of different isomeric structures. Structural models: Au yellow, C gray, H white. The energy difference of the 2-b isomer relative to the 2-a, and for isomers 4-b and 4-c relative to the 4-a isomer are given next to the geometric structures, with the values in parenthesis giving the zero-point energy corrected values.

including a zero-point-energy, zpe, correction) to form the global minimum structure 3-a. The subsequent dissociation of one C-H bond to form the hydrido-methyl complex 3-b is not only endothermic but also involves a transition state which is located 0.71 eV above the entrance channel ($\text{Au}_3^+ + \text{CH}_4$), with a total activation barrier of 1.47 eV (from the 3-a global minimum), or 1.36 eV when zpe-corrected. However, under the multi-collision conditions in the flow tube reactor it is likely that such an energy barrier can be overcome and that the hydrido-methyl complex can be stabilized by collisions with the He buffer gas.^[6a] In contrast, the dissociation of the second and third C-H bond involves higher barriers of 1.72 eV (1.56 eV, zpe-corrected) and 2.90 eV (2.67 eV, zpe-corrected), respectively, and these reactions are even more endothermic rendering the formation of the complexes 3-c and 3-d highly unlikely.

To gain insight into a possible cluster size dependency of this process we have also studied Au_2CH_4^+ and Au_4CH_4^+ and the corresponding Ar complexes. The results are compiled in Figure 3 which demonstrates that the experimental spectra obtained for the complexes without and with Ar are much alike. This indicates again that the Ar atoms have only a minor influence on the structural properties of these cluster complexes. The Ar-tagged complexes exhibit better resolved features, which will be considered below. Similar to the Au_3^+ case, the calculated minimum energy isomeric structures of Au_2CH_4^+ and Au_4CH_4^+ contain a non-dissociated methane molecule (2-a and 4-a)^[7a] while the hydrido-methyl complexes (2-b and 4-b) are higher in energy by 0.16 eV (0.05 eV with zpe correction) and 0.43 eV (0.35 eV with zpe correction), respectively. In addition, for Au_4CH_4^+ a second hydrido-methyl complex isomer (structure 4-c) has been found theoretically, which is 0.60 eV (0.53 eV, zpe corrected) higher in energy with respect to the lowest energy isomer.

The experimental IR-MPD spectra of both cluster complexes Au_2CH_4^+ and Au_4CH_4^+ show characteristic bands (I and VI for Au_2CH_4^+ , Figure 3a, second panel; I for Au_4CH_4^+ , Figure 3b, second panel) that can be clearly assigned to vibrations corresponding to the intact CH_4 molecule of the lowest energy isomer (highlighted in green). In addition, features II, III, and VII in the spectrum of Au_2CH_4^+ (Figure 3a, second panel) as well as feature II in the spectrum of Au_4CH_4^+ depicted in Figure 3b (second panel) correspond to the motions of the methyl group (blue) and the H atom

(red) of the hydrido-methyl complexes, respectively; the remaining signals in these IR-MPD spectra most likely contain contributions from both isomeric structures, and the presence and some contributions from isomer 4-c are conceivable. Additionally, the characteristic vibrational modes of the H atom bound to an Au atom – observed at 1640 cm⁻¹ for Au₂CH₄⁺ (labeled VII in Figure 3a, second panel) and at 1660 cm⁻¹ for Au₃CH₄⁺ (VII in Figure 1b, first and second panel) – shift to 1392 cm⁻¹ and 1525 cm⁻¹ for 4-b and 4-c, respectively, resulting in partial overlap with the spectral features of isomer 4-a.

Hence, the IR-MPD spectra of all three investigated gold clusters show characteristic spectral features, which clearly uncover the co-existence of two isomers - one corresponding to a complex with an intact, non-dissociated CH₄ molecule and the other corresponding to a hydrido-methyl complex, H-Au_x⁺-CH₃. This clearly demonstrates that small cationic gold clusters can selectively dissociate one C-H bond of methane which represents an important pre-requisite for any subsequent selective catalytic conversion of methane to more valuable products.

To conceive of this balanced catalytic action of the gold clusters, their electronic structure and the resulting interaction with methane has to be considered. The selective C-H-bond activation by gold clusters originates from the closed-shell nature of the gold atom d-shell, which due to relativistic effects becomes accessible for binding.^[3b, 13] The involvement of the gold d-orbitals (along with the gold p orbitals) in the binding of methane to gold clusters (mainly via the hydrogen atom s-type orbitals) has been detailed in a previous contribution.^[7a] The activation and cleavage of the first C-H-bond is then the result of an insertion of the binding gold atom into one C-H-bond of methane. This mechanism has been suggested to occur for gold clusters a long time ago,^[7c] yet it has previously been observed experimentally only for Pt⁺ in reaction with CH₄.^[14] A large difference between the Pt⁺ case and all other hitherto investigated atomic and metal cluster ions, lies in the observation that the reaction does not stop at the hydrido-methyl complex. Dehydrogenation proceeds yielding mostly the strongly bound and thermodynamically very stable metal-carbene complex M⁺-CH₂.^[3b, 15] In contrast, the complete filling of the d-orbitals of the gold clusters renders them less active regarding dehydrogenation reactions, in comparison with other heavy transition metals.^[7d, 16] Consequently, strictly only one C-H-bond is activated and cleaved, resulting exclusively in the gold cluster-hydrido-methyl complexes observed in the present investigation. These hydrido-methyl complexes are thermodynamically considerably less stable than metal-carbene complexes and thus they are ideally suited for further selective functionalization under thermal conditions, opening new vistas for catalytic transformation of methane into desired valuable products with possible chemical and energy-related applications.

Acknowledgements

We gratefully acknowledge the Stichting voor Fundamenteel Onderzoek der Materie (FOM) for the support of the FELIX Laboratory. The research leading to these results has received funding from the European Community's CALIPSO program. SML is grateful to the ESF Baden-Württemberg for a Margarete von Wrangell fellowship. The work of UL was supported by the Air Force Office of Scientific Research under Award No. FA9550-15-1-0519, and that of RNB by the Office of Basic Energy Sciences of the US Department of Energy (Grant No. FG05-86ER45234). Calculations were carried out at the GATECH Center for Computational Materials Science. Additional data can be found in the supplementary material.

Keywords: selective methane activation • C-H bond cleavage • gold clusters • ab-initio calculations • vibrational spectroscopy

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